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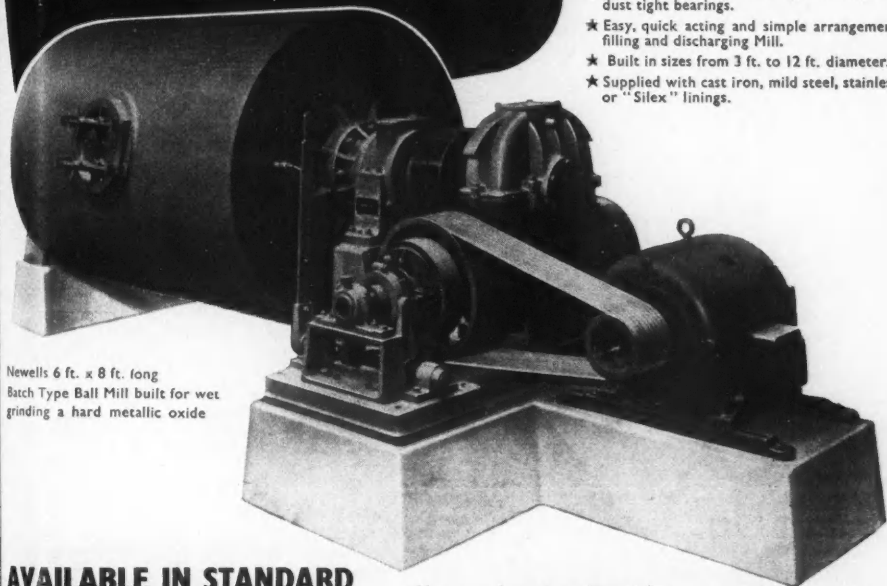
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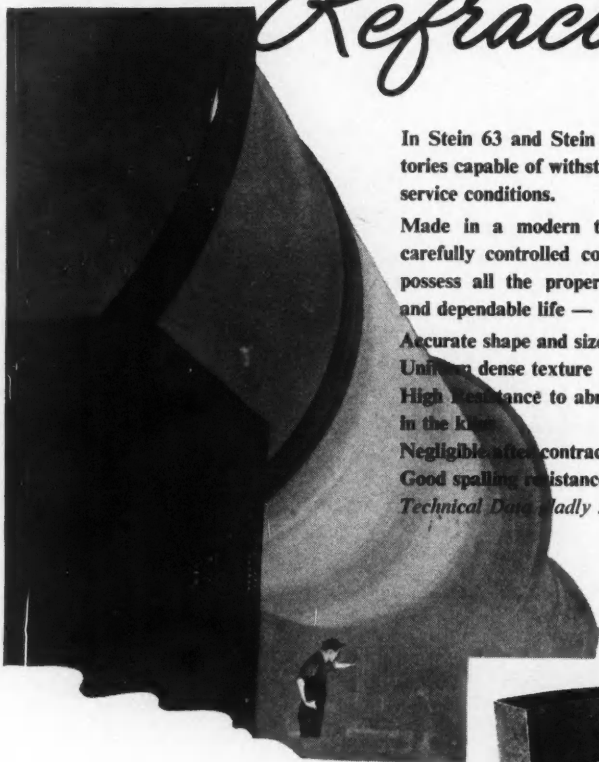
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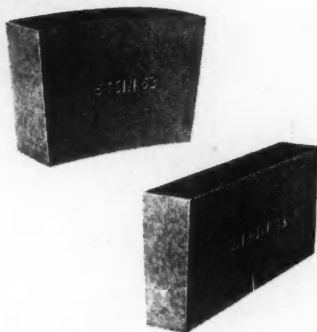
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A Large Rotary Kiln in France.

CAPACITY OF 1,000 TONS A DAY.

THE French cement company Lambert Frères & Cie is now operating a new rotary cement kiln (*Fig. 1*) with a capacity of 1,000 tons a day at their works situated on the right bank of the river Seine just outside Paris. It is thought that this kiln has the highest rate of production of any kiln in the world. Other plant at the works includes two washmills; two raw-material mills 6 ft. 6 in. by 24 ft., each driven by a 240-h.p. motor; two wet-process Unax kilns 9 ft. 10 in. by 8 ft. 10 in. by 9 ft. 10 in. by 328 ft. long, each with a capacity of 400 tons of clinker per day; four Unidan cement mills of which two are 7 ft. 2 in. diameter by 40 ft. long driven by 650-h.p. motors, and two are 7 ft. 10 in. diameter by 43 ft. long driven by 1,000-h.p. motors. The cement is packed in paper bags on three Fluxo rotary packing machines each with a capacity of about 1,600 bags per hour. All the mills are driven centrally through Symetro reduction-gears. After leaving the

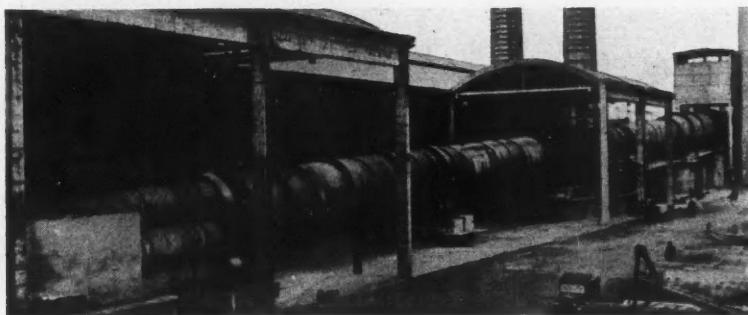


Fig. 1.—Kiln 445 ft. long in France.

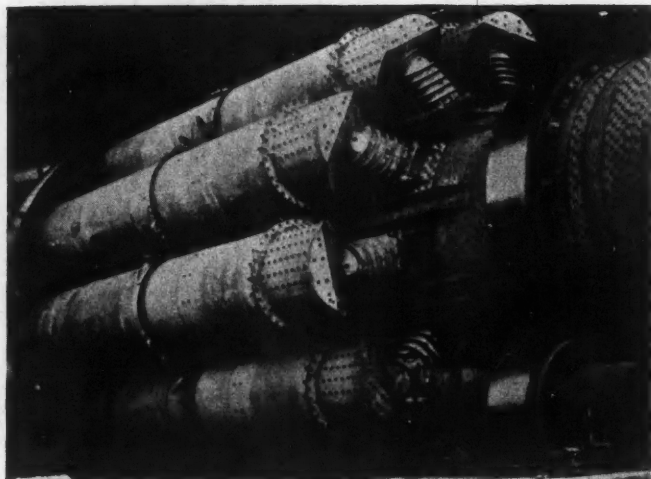


Fig. 2.—Cooling End of Kiln.

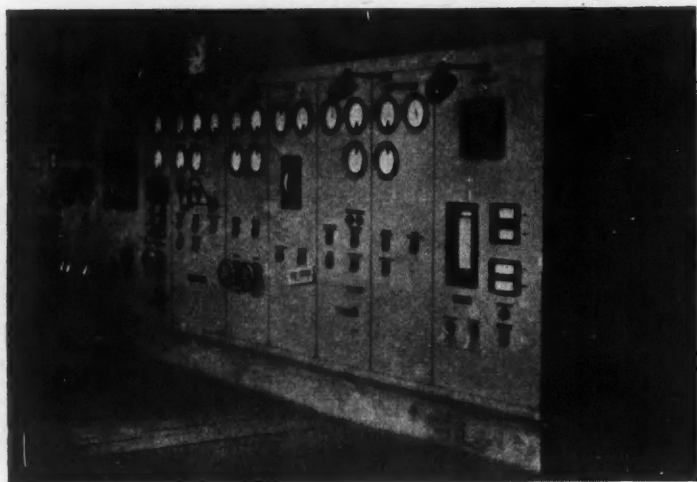


Fig. 3.—The Kiln Control Board.

mills, the cement is cooled in Smidth coolers and transported to the silos by Fluxo pumps.

The new Unax kiln, also supplied by Messrs. F. L. Smidth & Co., is provided with a planetary multi-tube cooler (*Fig. 2*) consisting of ten tubes. The kiln shell is 445 ft. long by 12 ft. 4 in. diameter with an extended diameter of 15 ft. 1 in. in the drying zone. It rests on six supports at an inclination of 5 in 100, and is partly welded and partly riveted. The cooler outlets for the new kiln are enclosed in a dustproof casing.

The raw materials consist of chalk (which is transported in barges from a quarry about 30 miles down the river) and clay which is excavated as the overburden of the company's gypsum quarry. On account of the presence of small quantities of gypsum in the clay, the water content of the slurry cannot be reduced to less than 41 per cent.

The new kiln is provided with a spiral-scoop feeder synchronized for the kiln

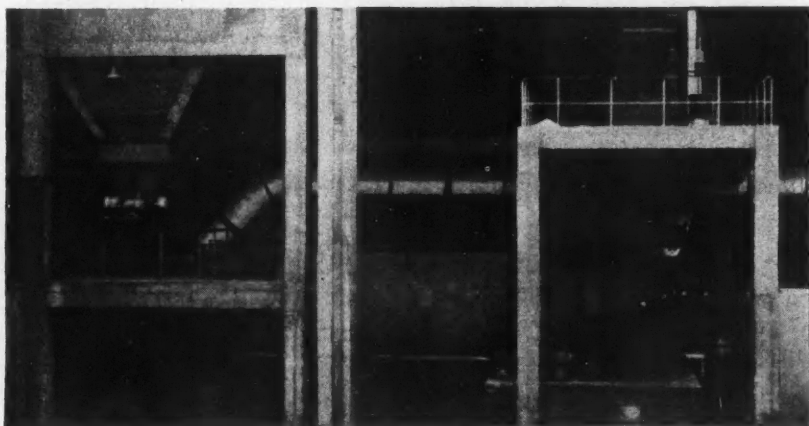


Fig. 4.—Mill for Simultaneously Drying and Grinding Coal.

speed, which is 1.32 revolutions per minute. The measurement and the full control of the slurry feed are done by instruments on a control panel at the burner's platform; this panel also contains indicators, recorders, and regulating devices for the control of the kiln (*Fig. 3*).

The fuel used is coal with 3 per cent. to 5 per cent. moisture content, 23 per cent. volatile matter and 22 per cent. ash content, and is ground in a direct-fired air-swept Tirax mill (*Fig. 4*) provided with a drying chamber and a rotary separator. The mill is 7 ft. 11 in. in diameter and 14 ft. 6 in. long with a 7-ft. 11-in. drying chamber, and rests on two slide-shoe bearings. It is driven by a 325-h.p. motor through a speed-reducer connected to the pinion-shaft of the mill. This mill is situated behind the burner's platform and is in line with the kiln.

The high-pressure fan for the primary combustion air is driven by a variable-speed motor of 120-h.p., and circulates the air through the mill, after which the air is used as primary air for the kiln. In order to avoid wear on the fan by passing the pulverized coal through it, the coal is precipitated in a cyclone before passing the fan, after which it is fed directly into the primary air. An extra fan and motor are installed as a stand-by. The raw coal is fed to the mill by two Pandan feeders from separate hoppers to allow for two different qualities of coal to be used at the same time. These feeders are automatic, constant weight being ensured by extracting, weighing, and recording bands. The mill feed is also controlled by the FolaPhone acoustic control system.

The kiln is equipped with a chain system in which the water content of the slurry is reduced from 41 per cent. to about 14 per cent. Below the chain system is a cross system of special design for further improvement of the heat exchange.

With a production of 1,000 tons a day the heat consumption is 1,475 kilo-cal. per kilogramme of clinker, or about 6,000,000 B.T.U. per ton. For short intervals the kiln has produced 1,050 tons per day, but, as no dust precipitator is installed, the dust loss seems to limit the production. Space is, however, available for electrical dust precipitators.

Accuracy of Test for Heat of Hydration of Portland Cement.

IN view of the fact that the calorimeter and the method of calculation specified in B.S. 1370 (1947) for the determination of the heat of hydration of low-heat Portland cement is almost the same as that required by standard specifications in the United States, the results of tests made at the National Bureau of Standards to establish the accuracy of the determination are of interest. The tests are described by Mr. E. S. Newman in the Bureau's Journal of Research for November 1950, and were made by the heat-of-solution method (Federal Specification SS-C-158b, 1946; A.S.T.M. C-186-49).

Three relatively inexperienced men each made six determinations of the heat of hydration of a sample of Portland cement. The results of their measurements were calculated by the method described in the Federal Specification and by two simpler reduced-observation methods. A statistical analysis showed that there were no significant differences between the measurements obtained by the three men. The reduced-observation methods gave acceptable results in the special tests, but the agreement of the methods of calculation was not so good when the methods were applied to routine tests. The two reduced-observation methods of calculation were based on the temperature of the calorimeter at 0, 20, and 40 minutes, and at 0, 25, and 50 minutes respectively.

The special tests indicate that the heat of hydration of Portland cement can be determined by the heat-of-solution method with a precision (that is, the standard deviation of a single determination) of about 3 calories per gramme at 7 days and 2 calories per gramme at 28 days. Better precision might be expected from experienced operators.

Suggested Principles of Low-pressure Steam Curing of Mortar and Concrete.

By A. G. A. SAUL, B.Sc.(Eng.)

ALTHOUGH much experimental work on the steam curing of cement and concrete at atmospheric pressure has been carried out during the past thirty years, the results are sometimes apparently conflicting. Many investigators have observed that some types of Portland cement respond to heat treatment better than other types; other investigators advocate optimum temperatures, duration of treatment, periods of waiting before treatment is started, or special curing cycles, but few of the recommendations agree. In this article are summarized some of the apparently conflicting results, and a manner is suggested in which they can be reconciled with results obtained by the writer in experimental work.

Previous Experimental Results.

Mr. R. W. Nurse¹ found that gain of strength of concrete is a function of the number of degrees of temperature above freezing point multiplied by the duration of the treatment. Treatment of given intensity (measured in degrees centigrade multiplied by hours) gave about the same strength irrespective of the maximum temperature or duration. For example, ten hours at 80 deg. C. is equivalent to 20 hours at 40 deg. C. and to 48 hours normal curing at 16 $\frac{2}{3}$ deg. C., since each product is a maturity period of 800 degrees-hours. Therefore "temperature-time," and not time alone, best describes the maturity of concrete exposed to varying temperatures. Mr. Nurse also found it unnecessary to delay the commencement of treatment for a period after mixing.

Dr. J. Brocard² cured cubes of Portland-cement paste by electricity and in water at 30 deg., 50 deg., and 75 deg. C. for periods of 6, 24, and 48 hours from the time of mixing, and found that in some cases the higher temperatures resulted in lower strengths. If it is assumed that there is no radical difference between steam and electrical or hot-water curing, this result conflicts with the observations made by Mr. Nurse.

Mr. P. H. Bates and Mr. R. L. Blaine³ cured specimens of mortar of four different Portland cements. Some of the specimens were immersed in water and some were above water which was brought to the boil in one hour and maintained thus for 16 hours. The specimens were tested at 24 hours, and at 3, 7 and 28 days, and it was found that the 28-days' strengths were much less than the strengths of specimens cured by standard methods. The 7-days' strengths were also less for some cements. It was found that slow-hardening cement gave greater strength than rapid-hardening cement. The specimens cured in water were at all ages weaker than those steam cured, but the specimens cured in water must have reached a temperature of 100 deg. C. within an hour, and the other specimens only began to be heated appreciably when steam began to be generated. In neither case was the gain in strength in accordance with Mr. Nurse's conclusions.

Mr. J. J. Shideler and Mr. W. H. Chamberlin⁴ cured three series of specimens at various temperatures in a steam chamber. In two series the specimens were placed in the chamber one hour or less after mixing, and in neither case did the strengths at various ages agree with Mr. Nurse's results, being relatively less at greater age at the higher temperatures. In the third series, treatment was started at varying times up to twelve hours after mixing, all specimens being removed from the chamber 24 hours after mixing. Postponement of treatment produced greater strength with age, especially at the higher temperatures, but the later the start the less the length of the treatment and the less the maturity-period measured in degrees-hours. Therefore two opposing variables were introduced, as a result of which the optimum temperature and duration of treatment suggested were 55 deg. to 74 deg. C. for eight hours. Analyses of the results in terms of temperature-time show that, when treatment started at the age of six hours or later, the results agreed with Mr. Nurse's conclusion; if at four hours, there was a relative falling off of strength at the highest temperature (85 deg. C.); if at two hours, a greater falling off occurred at 85 deg. C. and a considerable falling off at the next highest temperature (74 deg. C.); and if at one hour or less the treatment at the lowest temperature (38 deg. C.) still produced results consistent with those of Mr. Nurse, but at all other temperatures there was a progressively greater falling off with increasing temperature.

Mr. G. A. Mansfield⁵ recommends for the curing of concrete blocks a period of one to two hours before treatment, then a period with the steam fully on (which must not be continued beyond the point at which the concrete reaches the temperature of the curing chamber), and thereafter a prolonged cooling or soaking period. Tests gave best results with a maximum temperature of 77 deg. C. and a steaming time of 1 hour 25 minutes. Pressed concrete blocks made with very dry concrete have a relatively large exposed area, and Mr. Mansfield laid importance on the loss of moisture through evaporation. If the initial rise in temperature is too rapid, loss of strength on prolongation of the treatment may be due to other causes, as are discussed later.

Reconciliation of Apparently Conflicting Results.

The following inferences have been drawn from a series of steam-curing experiments at atmospheric pressure made by the writer, and are considered in conjunction with the results quoted.

CASE A.—When concrete does not reach certain temperatures within certain times after mixing, for example, 50 deg. C. within 1½ to 2 hours and 100 deg. C. within 5 to 6 hours, depending on the type of cement, the following apply:

- (a) The strength at a given maturity (temperature-time) is approximately the same whatever the curing cycle; this is in agreement with Mr. Nurse's conclusions.
- (b) The strength increases subsequently in the normal manner, but tends to be less than that of concrete cured normally and of the same age after about seven days; for example, the difference may be 6 per cent. to 12 per cent. at 28 days.
- (c) With the concretes tested, the strength increased with maturity in the normal manner when the treatment was prolonged to nine hours, and no ill effects were observed.

CASE B.—When the temperature is raised rapidly soon after mixing (for example up to 100 deg. C. in one hour), the following apply: (a) The gain of strength is more rapid than in Case A in the first few hours, but thereafter falls off. (b) The strength does not increase subsequently in the normal manner. The loss of strength compared with concrete treated as in Case A is most pronounced at about seven days, there being a tendency to regain strength thereafter. (c) The tendency to recover strength is less at higher temperatures and when treatment at the maximum temperature is prolonged.

It will be noted that some of the characteristics of the concrete in Case B are the opposite of those in Case A.

CASE C.—When the initial rate of rise of temperature lies between the limits in Cases A and B, the concrete has characteristics which lie between those of the concrete in Cases A and B.

CASE D.—A wide range of Portland cements responds similarly to steam curing at atmospheric pressure, although the rapid-hardening cements tested required a slower initial rise in temperature.

According to the foregoing, two types of concrete can be produced by steam curing at atmospheric pressure: Concrete A is relatively normal and is affected substantially in its gain of strength only by its maturity as measured by temperature-time. Concrete B is adversely affected as regards strength mainly by the initial rate of rise of temperature and to a less degree by the intensity and duration of its treatment. High temperature and prolongation of treatment are beneficial in Case A but deleterious in Case B.

The apparently conflicting results of various investigators may now be explained. The investigators who delayed the commencement of treatment or used a low initial rate of rise of temperature obtained concrete A, and reach the same conclusion as Mr. Nurse. Investigators who placed their specimens in a heated atmosphere directly after mixing produced concrete B, and are in agreement with Dr. Brocard. Those who adopt a medium rate of rise of temperature or delay treatment for one to four hours and then place their specimens in a chamber controlled at various temperatures obtain concrete A at low temperatures and concrete B at high temperatures, and an intermediate type of concrete at intermediate temperatures. They may find, like Mr. Bates and Mr. Blaine, that some cements give better results than others or, like Mr. Shideler and Mr. Chamberlin and others, that there appear to be optimum curing cycles.

Results of the Tests.

The tests made by the writer include thirty-one different treatments of six cubes of each of two mixtures. Rapid-hardening Portland cement, ordinary Portland cement, and special low-alumina Portland cement were used, and two water-cement ratios were employed. The results obtained for the rapid-hardening cement concrete with the higher water-cement ratio are shown in *Figs. 1 and 2*. *Fig. 3* shows the results for rapid-hardening and ordinary Portland cement concrete with both water-cement ratios. The diagrams illustrate, however, tendencies typical of the three types of cement with both the water-cement ratios.

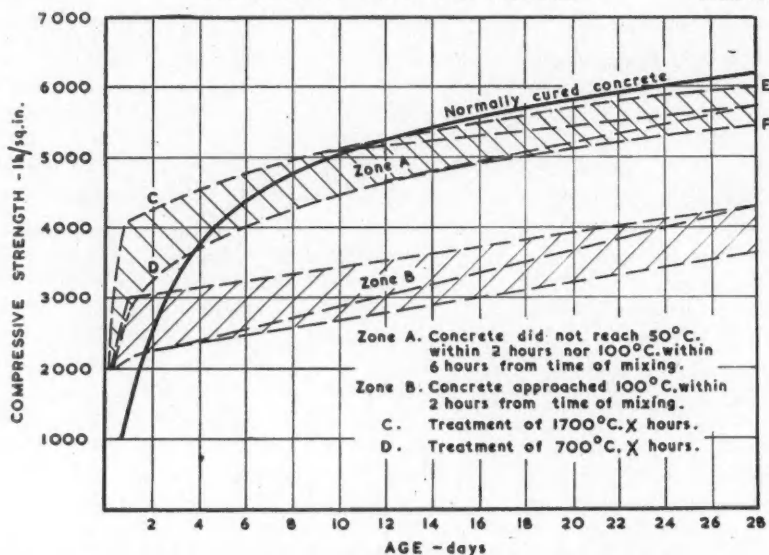


Fig. 1.—Gain of Strength with Time after Steam Curing at Atmospheric Pressure. Rapid-hardening Portland Cement Concrete 1:5½. Water-Cement ratio 0.5.

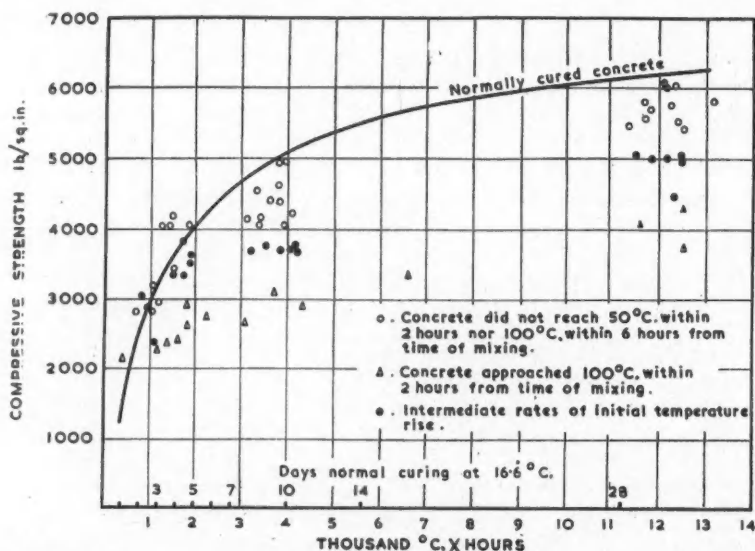


Fig. 2.—Gain of Strength with Maturity. Rapid-hardening Cement Concrete 1:5½. Water-Cement ratio 0.5.

Fig. 1 shows the gain of strength with time of specimens subjected to various curing treatments during the first 24 hours. The treatments include a delay of commencement of treatment of from one to six hours after mixing, various rates of heating and cooling, maximum temperatures of 60 deg. to 100 deg. C. maintained for periods up to eight hours, and treatment of from 700 to 1,700 degrees-hours. Specimens subjected to a slow initial rise of temperature as in Case A have strengths at ages up to 28 days in zone A. For the first few days the strengths lie between points C and D, depending on the treatment measured in degrees-hours, but later are scattered between points E and F. Specimens subjected to a rapid initial rise of temperature as in Case B have strengths in zone B, the specimens given the least intensity of treatment showing recovery at 28 days.

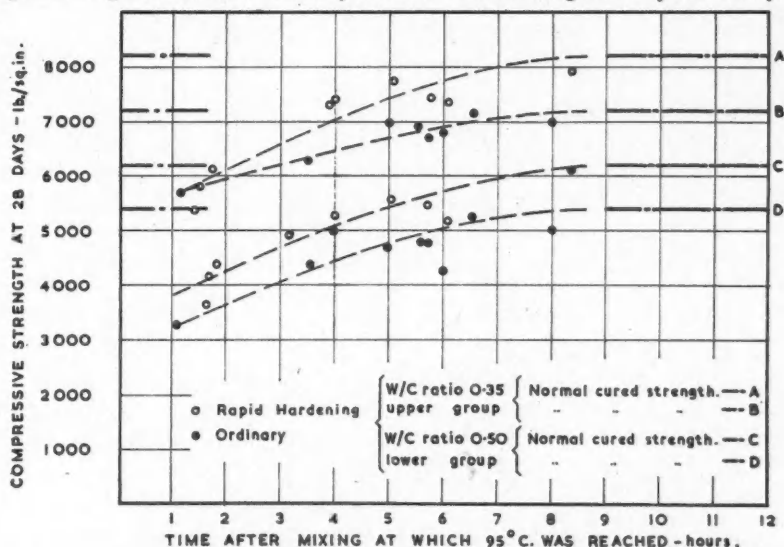


Fig. 3.—Steam Curing at Atmospheric Pressure. Effect on Strength of Concrete of Rate of Initial Rise of Temperature.

Intermediate rates of rise of temperature gave results lying between zones A and B.

These results are illustrated better in Fig. 2, where they are plotted against maturity in degrees-hours. It will be noted that the specimens in Case A tend to conform to the results for normally cured concrete, but are slightly weaker after about seven days. Specimens tested 24 hours after treatment were nearly dry, whereas the others were wet when tested. Allowance should be made for this condition by a relative reduction of the strength at 24 hours, which might therefore be less than the strength of normally cured concrete of equivalent maturity.

Fig. 3 shows the effect of the initial rate of rise of temperature on the 28 days' strength, which is more marked for rapid-hardening Portland cement than for

ordinary Portland cement. This relationship is approximate only, since these specimens did not all reach 95 deg. C. in comparable manners and those in which the temperature of 95 deg. C. was reached in two hours or less were also affected by the intensity and duration of the treatment.

The results of the tests suggest that a strength as great as that of normally cured concrete can be attained at any age by steam curing at atmospheric pressure if a very slow rise of temperature is adopted or the treatment is postponed sufficiently. The practical value of such treatment is, however, probably limited. The results suggest also that the deficiency of strength at a later age is a function of the rate of rise of temperature from the time of mixing, although such deficiency assumes serious proportions only if a critical rate, which varies slightly with different cements, is exceeded.

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The Transport of Cement in Special Sacks.

SACKS containing about $\frac{1}{2}$ ton of cement are in use in Sweden. An empty sack is suspended so that its bottom is a few inches above the level of the floor of a motor lorry or railway wagon immediately below the outlet of the silos at the cement works. The sack is kept open by a metal ring inserted vertically in its mouth, and is filled through a trunk connected to the outlet valve and extending about 18 in. into the sack. When the sack is filled, the ring is removed, the sack is lowered on to the vehicle, and is closed by four cords attached permanently to the outside of the sack. The time taken to fill six sacks, containing about 3 tons, and place them on a lorry is 15 to 20 minutes, and two men are employed.

Upon arrival at the place of delivery, the four cords, which have metal eyelets at their ends, are attached to a hook suspended from a $\frac{3}{4}$ -ton electric hoist travelling on a cat-head. The sack is lifted off the lorry, the hoist is taken along the cat-head into the store, and the sack is lowered on to the floor of the silos and tipped (by a special tilting gear) so that the cement is emptied into the silos. The time taken to lift six sacks off a lorry and empty them into a silo by the method described is about 15 minutes.

The Uses of Expanding Cement.

IN this journal for January 1947 some notes were given on the expansive cement developed in France by M. Henry Lossier. This type of cement has been used in the repair of a reinforced concrete bridge over the river at St. Julien, France, the cellular arch of which was damaged during construction as the result of the settlement of a temporary pier. The span of the arch is 328 ft., the rise-to-span ratio is about one-tenth, the width is 20 ft. 8 in., and the thickness varies from 4 ft. 11 in. to 7 ft. 6 in. The thickness of the walls of the three cells is 10 in. The abutments are on rock.

The settlement of the pier while the arch was being constructed in segments caused the arch to twist, and cracks occurred in the segment next to the left-hand

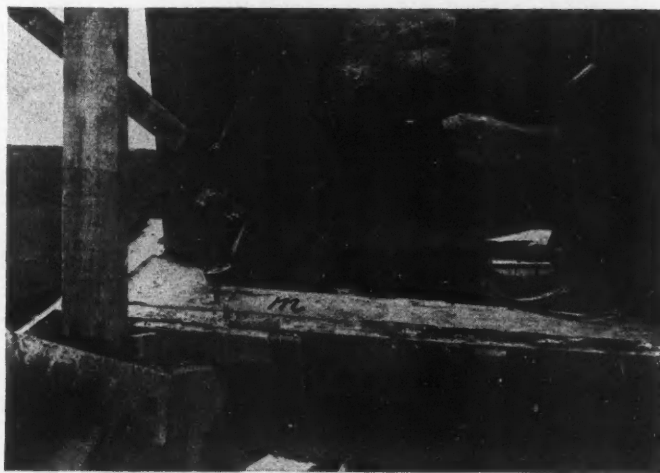


Fig. 1.

abutment. Due to the elastic settlement of the centering, the arch was partly supported on the abutments. At the left-hand abutment, the arch was supported only through the intrados slab, since the crack at the springing destroyed any support above the slab. To restore the arch to the original condition, it was proposed to exert a thrust between the arch and the abutment. Two methods were considered, the first being to impose the thrust by means of jacks placed in a cavity cut in the arch; while the jacks were in operation, the cavity would be filled with concrete, the jacks would be removed when the concrete had hardened, and the space they occupied also filled with concrete. The second method was to insert a segment of expanding-cement concrete, and this method was adopted because it would give a uniformly distributed pressure, which would attain its maximum

only after several days, instead of the isolated and rapid compressive actions of the jacks. The four operations of installing the jacks, concreting between the jacks, removal of the jacks, and the filling of the spaces which they occupied, were replaced by one operation, and the absence of mechanical devices reduced the possibility of unforeseen difficulties. The method was carried out as follows.

The concrete of the arch was cut out at right-angles to the crack at the springing for the entire width of the arch and for a length of about 20 in. In the cut thus made, the segment was constructed with concrete containing 1,000 lb. of expanding cement. The cement was made so that a pure paste in the free state would swell, upon wetting, 1.2 per cent. to 1.5 per cent. linearly. To ensure that the concrete was moistened sufficiently to cause the tendency to expand, holes of $1\frac{1}{2}$ in. diameter were made by steel bars which were removed before the concrete set. A temporary mortar dam (m) retained a pool of water (E) on the segment (*Fig. 1*) which maintained the moistening for twelve days, which was the period required for the expansive force to be developed. Instruments recording the effects were attached at several points of the segment.

Cubes of the expanding-cement concrete made at the site had compressive strengths of 6,941 lb. to 7,282 lb. per square inch at 90 days, compared with a calculated strength of 4,580 lb. per square inch and the working compressive stress of 1,280 lb. per square inch. The actual strengths (in lb. per square inch) at other ages were 4,082 to 4,409 at eight days and 5,405 to 7,823 at 28 days. The centering was removed thirteen days after the concreting of the segments. The work was carried out by Etablissements Fourre et Rhodes to the design of Monsieur H. Lossier.

Raw Materials in Cement Manufacture.

THE Ministry of Local Government and Planning has imposed conditions to prevent unnecessary defacement of the countryside in connection with the working of chalk and marl at the Norman Cement Works in Cambridgeshire. Tree-planting and landscape schemes are to be agreed between the owners and the County Council, and all plant and machinery are to be removed when they are no longer needed. The Ministry points out that in the past twenty-five years the annual production of cement has increased from about 3,000,000 to nearly 9,500,000 tons, and the demand shows no sign of abatement. Future planning of the industry must include provision for increasing output, and in the opinion of the Ministry the securing of reserves of raw materials to provide a working life for cement works of up to one-hundred years is desirable.

The Norman works has recently been reconstructed by the British Portland Cement Manufacturers, Ltd., at a cost of £340,000.

Hydrothermal Reactions in the System $\text{CaO-SiO}_2\text{-H}_2\text{O}$.

IN the "Magazine of Concrete Research" for July, 1950, Dr. H. F. W. Taylor, Ph.D., B.Sc., and Mr. G. E. Bessey, M.Sc., F.R.I.C., review investigations made on the lime-silica-water system under hydrothermal conditions. The following is an abstract of the paper, which gives the sources of the views expressed and a bibliography.

The hydrated calcium silicates appear entirely as amorphous or gel-like materials in cement hydrated at ordinary temperatures, but under hydrothermal conditions the lime-silica-water system (C—S—H system) yields a number of distinctive crystalline compounds, at least one of which has been detected in steam-cured Portland cement mortar. Studies of this system have been mainly studies of the natural minerals, of the hydration reactions and the compounds formed at temperatures up to 30 deg. C., and of hydrothermal reactions above 100 deg. C. Little has been done to link together the investigations of the amorphous materials formed at ordinary temperatures and those of the crystalline products formed at the higher temperatures, and hardly any work has been reported on temperatures between 30 deg. C. and 100 deg. C.

Hydrothermal reactions have mostly been carried out in one of two ways, described as the bomb and the autoclave methods. In the former, the solid reactants are usually placed in contact with water in a closed steel bomb which is maintained at a given temperature from 100 deg. to 500 deg. C., the quantity of water being sufficient to ensure the presence of both liquid and vapour phases at all temperatures below the critical temperature (374 deg. C.). In the C—S—H system the solubilities are small, and the partial pressure developed below the critical temperature is essentially the saturated vapour pressure of water at the operating temperature, and is therefore independent within wide limits of the degree of filling of the bomb. The reaction then occurs almost completely in the condensed phase, and increase of pressure by addition of compressed nitrogen has been shown to have no significant effect on the course of the reaction.

The autoclave method has been used at temperatures up to 350 deg. C. The reactants, either dry or in the form of a slurry, are treated with saturated steam at a constant pressure, and are thus in contact with only a small amount of the liquid phase.

Investigators have apparently used only one or other of the methods, and it is not easy to generalize on the different results obtained. The formation of metastable products is more likely to occur when the reaction takes place out of contact with the liquid phase, and it is likely that this condition may favour the formation of products richer in lime and poorer in water of hydration than when the reaction mixture is in contact with liquid.

Most investigators have difficulty in obtaining reproducible results. Some investigators have concentrated on the attainment of true equilibrium and the

formation of thermodynamically-stable products, which are possible in hydrothermal reactions, at least at the higher temperatures, as shown by investigations on the system $K_2O-K_2SiO_3-H_2O$ in the range 200 deg. to 1000 deg. C. On the other hand, the investigation of less stable species and the conditions of their formation may also be of the greatest interest, because they are relevant to the problem of cement hydration. The formation of metastable products is not unlikely, because of the relatively low temperatures at which the hydrated products are formed and because the anhydrous calcium silicates readily yield solutions strongly supersaturated with lime.

The Silica-rich Part of the System.

Observations of the silica-rich part of the system in which the proportion of water used in the experiment appears to be 0.5 g. of solid with up to 10 ml. of water, showed the formation of a number of crystalline phases. The time necessary to effect crystallization varied from 4 days at the higher temperatures to 60 days or more at 150 deg. C., the lowest temperature used. Cristobalite was formed at very small lime contents. Increase in the ratio of lime to silica yielded, at temperatures above about 400 deg. C., successively pseudo-wollastonite, wollastonite, and $\beta-C_2S_2$, and, at temperatures below about 400 deg. C., gyrolite, $C_4S_5H_6$, xonotlite or CSH, and foshagite. With the exception of $\beta-C_2S_2$, the products were obtained from initial materials which were either glasses or hydrous precipitates obtained by adding lime-water to dilute solutions containing lime and silica. Experiments carried out to establish the stability of products showed that pseudo-wollastonite was partially converted to wollastonite at 500 deg. C. Xonotlite was unchanged at 390 deg. C.; $\beta-C_2S_2$ was obtained by the action of water at 500 deg. C. on the common or α -form, which is metastable. The β -form is stable in air at temperatures below 1024 deg. C.

The compound of α -cristobalite appears to form readily from silica-rich mixtures with neutral or weakly alkaline solutions under hydrothermal conditions. It seems that the limit of lime content above which a hydrated calcium silicate appears as a second phase with the cristobalite must be small, since solid lime is not likely to exist as such in equilibrium with cristobalite.

The formation of wollastonite (CS), xonotlite (C_2S_2H), and the compound (CSH) from mixtures of CSaq. composition at successively lower temperatures is of interest. Wollastonite has recently been obtained at 405 deg. C. Xonotlite has been prepared from hydrous mixtures of its own C/S ratio at 150 to 200 deg. C. and at 300 to 350 deg. C., and from lime and quartz at 180 to 200 deg. C.

The water contents of preparations obtained from mixtures of CSaq. composition and dried at 100 deg. C. decrease with the temperature of preparation over a range of 130 to 290 deg. C. Natural crestmoroite has been described as zeolitic, with a water content between 0.5 and 1.5 mols.. It is thus possible that water in excess of 0.25 or 0.20 mol. is absorbed or expelled without fundamental change in crystal structure. On the other hand the X-ray data for xonotlite, crestmoroite, and CSH, while showing certain similarities, appear to indicate that distinct hydrates exist, and the change of combined water content with

increasing temperature of preparation may be due to the presence of mixtures of the compounds. Since there is considerable evidence that a definite monocalcium-silicate-hydrate can be formed at room temperature, further investigation of this question is of interest in connection with the hydration of Portland cement.

At C/S ratios between 1 and 2 either xonotlite or hydrates of C_2S , according to the temperature and C/S ratio, are obtained initially, but if the reaction times exceed eight days a new product, considered to be C_3S_2H , is obtained and it may be foshagite. On the other hand, at temperatures around 150 deg. C. a product considered to be afwillite has been obtained from mixtures of similar composition, but since some properties of afwillite are very close to those of C_2S α -hydrate, it is probable that the latter compound had actually been produced. The possibility that a C_3S_2 -hydrate forms at relatively low temperatures cannot, however, be overlooked.

The Lime-rich Part of the System.

The conditions of formation of the compounds obtained from mixtures of initial C/S-ratio of 2 or more, appear to be less clearly defined than in the case of the more acid mixtures; it seems possible that a variety of metastable products can be obtained under slightly varying conditions, but it is also possible that each of the compounds may have stable ranges of temperature and composition. The compounds which have been identified are considered in the following. Other products have also been observed in this part of the system.

TRICALCIUM-SILICATE-HYDRATE (C_3SH_2).—This compound has been prepared from C_3S at temperatures between 150 deg. and 500 deg. C. At lower temperatures, partial or total hydrolysis to C_2S - α -hydrate takes place, although the observed transition temperature varies from 120 deg. to 200 deg. C. C_3SH_2 has also been obtained from C_3S in the presence of additional lime and from hydrous mixtures of initial C/S-ratios of 3 or 4 at 275 deg. C. and over. At temperatures of 300 to 350 deg. C. only, hydrates of C_2S and not C_3S have been obtained from lime-silica mixtures, while only a monocalcium silicate having up to 3 mols. of absorbed lime was found by one investigator. The water content is from 1.3 to 2.0 mols. The correct formula may be C_3SH_2 with 0.5 mol. of water more easily lost than the remainder, and the structure may be analogous to that of norbergite, $Mg_3SiO_4(OH,F)_2$. The bulk of the water is undoubtedly held very tenaciously and appears to be driven off only at 900 deg. C., when breakdown to a form of C_2S and CaO takes place. Some investigators report that hydrolysis occurred on treatment with water and that equilibrium was attained much more rapidly than with anhydrous compounds, but others find the reaction to occur very much more slowly than that of anhydrous C_3S and do not find much hydrolysis after 70 to 100 days' shaking. The apparently inert character of this hydrate is remarkable.

DICALCIUM SILICATE α -HYDRATE (HYDRATE A OR I) ($C_2SH_{1-1.26}$).—This compound was first isolated from steam-cured Portland cement mortar. Its formation is attributed partly to hydration and hydrolysis of the cement constituents, and partly to reaction between lime liberated from the cement and silica sand. It

has since been obtained from lime with silica gel or quartz, and from hydrous mixtures of C_2S -composition at temperatures usually below about 200 deg. C., and from β or γ C_2S under similar conditions. The water content is not known with certainty. The formula $C_{10}S_5H_6(C_2SH_{1.2})$ has been proposed, and water contents of 1.1 to 1.25 mols. have been found. The compound appears to be only slowly dehydrated in air at 450 deg. C., but ignition at 900 deg. C. yields βC_2S . It is stable towards aqueous solutions of Na_2SO_4 , $CaSO_4$, or $NaOH$, but is attacked slowly by $MgSO_4$ or Na_2CO_3 and rapidly by dilute acids or ammonium salts. These reagents attack steam-cured Portland cement mortar similarly and it is likely that the formation of this compound in such mortar is partly responsible for the improvement in properties.

DICALCIUM-SILICATE- β -HYDRATE. (HYDRATE B, OR II) (C_2SH) .—Most artificial types of this product are obtained from mixtures of lime and silica. C_2S β -hydrate does not seem to form very readily from β or γ C_2S . Most preparations of this substance from lime-silica mixtures have been made at temperatures between 150 and 250 deg. C. One preparation was from βC_2S at 290 deg. C., and the formation of C_2S β -hydrate from βC_2S is also reported. Natural hillebrandite is unaltered by 11 days' treatment in an autoclave at 160 deg. C., and it may be that it is a stable, rather than a metastable, product under these conditions. On ignition at 900 deg. C., a mixture of β and γ C_2S is produced.

DICALCIUM-SILICATE- λ -HYDRATE (HYDRATE C OR III) $(C_2SH_{0.3-1.0})$.—This compound has been obtained from β - or γ - C_2S at temperatures rather higher than those used to produce the α or β hydrates. The γ -hydrate is the most usual product above 170 deg. C., and has been obtained at about 190 deg. C., although some investigators obtained the α -hydrate at 200 deg. C., and the γ -hydrate only at 250 deg. C. and over. There appears to be no clear record of the formation of C_2S γ -hydrate from lime-silica mixtures, although it has been found that it could be obtained from β - C_2S at 250 deg. C. in the presence of up to 2 mols. of added lime. The water content of C_2S - γ -hydrate varies between 0.3 and 1.0 mol. The compound may be a hemihydrate, possibly analogous to bertrandite ($Be_4Si_2O_7(OH)_2$).

Conclusions.

The large number of different compounds in the C-S-H. system, the very low solubilities, and the resulting difficulty of obtaining well-crystallized products or of ensuring equilibria, make the system extremely difficult to investigate. The existence of the following definite phases are reasonably established: C_3SH_2 , $C_2SH_{1-1.25}$ (α -hydrate), C_2SH (β -hydrate; hillebrandite), $C_2SH_{0.3-1.0}$ (γ -hydrate); $C_3S_3H_3$ (foshagite), $C_3S_2H_3$ (afwillite), C_5S_5H (xonotlite), CSH (crestmorite?), $C_4S_5H_5$, $C_2S_3H_2$ (gyrolite), and CS_2H_2 (okenite). Several other hydrates have been reported, but their identity cannot yet be regarded as established. It is also not yet known whether the apparently amorphous or gel materials formed at ordinary temperatures are distinct hydrates, or whether they are the same as some of those listed but with water absorbed owing to their large surface area. Very little has been done to relate the observations at atmospheric temperatures to those made at above 100 deg. C.

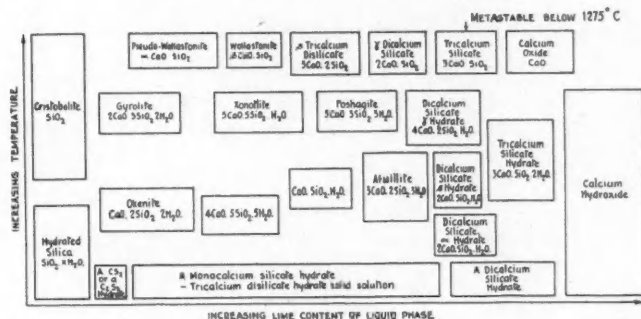


Fig. 1.

Some indications are available of the conditions under which certain of these compounds are formed, and the probable relative positions of the fields of stability in relation to temperature and to the lime-concentration of the liquid phase with which they must achieve equilibrium are indicated in *Fig. 1*. None of the phase boundaries has, however, yet been determined; in many of the investigations of the system there has indeed been little consideration of the implications of the phase equilibria. More work is necessary before even the conditions of stable equilibria can be defined; the extent to which metastable equilibria can occur under hydrothermal conditions is largely unknown.

The identity of many of the compounds can only be established by their X-ray diffraction patterns, because of their close similarity in optical properties and their occurrence only in microcrystalline or apparently amorphous form. Definite data are now available for most of them.

United States Standard for Sulphate-Resistant Portland Cement.

In the A.S.T.M. Standard Specification for Portland cement (C150-1949) some revisions are made to the requirements for cement (Type V) having high sulphate resistance. No limiting percentage of Al_2O_3 and Fe_2O_3 and ratio of these oxides are specified as was the case in previous standards, but a limit of 20 per cent. is set for the amount of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ plus twice the amount of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. The omission of the limiting ratios of Al_2O_3 and Fe_2O_3 also applies to Portland cement of moderate sulphate resistance and moderate heat of hydration (Type II). The minimum tensile strength of cement of Type V is increased to 250 lb. and 325 lb. per square inch at seven and 28 days respectively, and the minimum compressive strengths to 1500 lb. and 2200 lb. per square inch at seven and 28 days respectively.

The Cement Industry Abroad.

Belgium.

THE first kiln, about 480 ft. long, has started production at the new works at Lixhe of S.A. Cimenteries et Briqueteries Réunis. A similar kiln is being installed, and a third is contemplated. Each kiln has a capacity of 200,000 tons of cement a year.

Japan.

UNDER a plan submitted to the Government of Japan, the production of Portland cement is to be 4,800,000 tons in the year 1951, 5,150,000 tons in 1952, and 5,500,000 tons in 1953.

Finland.

THE production of Portland cement in Finland in the year 1950 was 743,000 tons. This is a record, and compares with 656,000 tons in 1949.

Switzerland.

THE consumption of cement in Switzerland in the year 1950 was 1,070,000 tons, an increase of 11 per cent. over the previous year, and a record for any year.

Mexico.

THE production of Portland cement in Mexico in the year 1950 was 1,290,000 tons, compared with 1,177,000 tons in 1949 and 1,080,000 tons in 1948.

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Specifications for Cement in the Netherlands.

THE standard specifications for cement and some types of lime, which were last published in 1933, were re-issued with some alterations in September, 1950. The revised specifications relate to ordinary and rapid-hardening Portland cement (N481), high-alumina cement (N482), ordinary and rapid-hardening iron Portland cement (N483), blastfurnace cement (N484), ordinary and rapid-hardening slag lime (N485; previously called slag cement), natural cement (N486), and two types of trass Portland cement (N618; previously called trass cement). The standard for cement-lime (N487) is now obsolete.

The principal alterations are the inclusion of strength tests of ordinary cements at three days so that an indication of the quality of the cement can be obtained before results at seven days are available, and some increases in the strengths of the ordinary cements and in the fineness of several cements. Table I gives the minimum strengths and maximum residues required. The initial setting time for all the materials is not less than one hour. The insoluble residue must not exceed

TABLE I.—REQUIREMENTS OF REVISED NETHERLANDS SPECIFICATIONS.

Material	Tensile Strength ⁽¹⁾			Compressive Strength ⁽¹⁾			Fineness (Maximum Residue)	
	Age in days			Age in days			Size of aperture in mm.	
	3	7	28	3	7	28	0.09	0.21
Portland Cement :							Per cent.	Per cent.
Ordinary	242* (17)	299* (21)	384 (27)	2489* (175)	3556* (250)	4623 (325)	15	—
Rapid hardening	327 (23)	384 (27)	455 (32)	3556 (250)	4978 (350)	6045 (425)	10	—
High-alumina cement	398 (28)	427 (30)	455 (32)	6401 (450)	6756 (475)	7112 (500)	14	—
Iron Portland Cement:								
Ordinary	242* (17)	299* (21)	384 (27)	2489* (175)	4556* (250)	4623 (325)	15	—
Rapid Hardening	327 (23)	384 (27)	455 (32)	3556 (250)	4978 (350)	6045 (425)	10	—
Blastfurnace cement:								
Ordinary	242* (17)	299* (21)	384 (27)	2489* (175)	3556* (250)	4623 (325)	10	—
Rapid Hardening	327 (23)	384 (27)	455 (32)	3556 (250)	4978 (350)	6045 (425)	8	—
Slag lime :								
Ordinary	—	185* (13)	356 (18)	—	1849* (130)	2560 (180)	18	2
Rapid Hardening	—	356* (18)	327 (23)	—	2845* (200)	3911 (275)	10	1
Natural cement ..	—	—	—	—	2133 (150)	3556 (250)	—	5
Trass Portland cement ..	—	299* (21)	384 (27)	—	3556* (250)	4623 (325)	8	—

⁽¹⁾ Strengths are given in pounds per square inch; values in brackets are in kilogrammes per square centimetre. Tests are made on specimens of 1 : 3 mortar after storage of 1 day in air and remainder in water.

* Optional tests.

3 per cent. except in the cases of slag lime, natural cement, and trass Portland cement for which no limit is given. Other requirements are given in the following.

ORDINARY AND RAPID-HARDENING PORTLAND CEMENT.—The ratio

$$\frac{C}{S + A + F}$$

must not be less than 1.7, the MgO-content must not exceed 5 per cent., and the SO₃-content must not exceed 3 per cent. (previously 2½ per cent.).

HIGH-ALUMINA CEMENT.—The minimum tensile strength is increased. The MgO-content must not exceed 5 per cent., and the SO₃-content must not exceed 2½ per cent.

BLASTFURNACE-SLAG CEMENTS AND LIME.—The ratio of Portland cement to blastfurnace slag in iron Portland cement is 7 : 3. In blastfurnace slag cement the amount of Portland cement must be from 15 per cent. to 69 per cent., and the amount of blastfurnace slag from 85 per cent. to 31 per cent. The only chemical requirement for these cements is that for the slag the ratio

$$\frac{C + \text{MgO} + \frac{A}{3}}{S + \frac{2A}{3}}$$

must not be less than unity. The chemical requirements of slag lime are that the MgO-content must not exceed 5 per cent. and the SO₃-content must not exceed 3 per cent.

NATURAL CEMENT.—The maximum amount of MgO is 5 per cent. and of SO₃ 2½ per cent.

TRASS PORTLAND CEMENT.—Two types of trass Portland cement are specified, one containing 30 per cent. of trass and 70 per cent. of Portland cement, and the other 40 per cent. of trass and 60 per cent. of Portland cement. The CaO-content of the former type is 47 per cent. (± 2 per cent.), and of the latter 41 per cent. (± 2 per cent.).

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